CHAPTER IV

RESULTS AND DISCUSSION

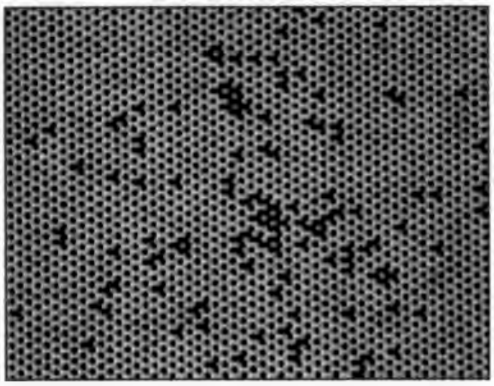
4.1 Screen quality from buffered slurry

4.1.1 By KH_2PO_4 and Na_2HPO_4 buffer solution pH 7.0

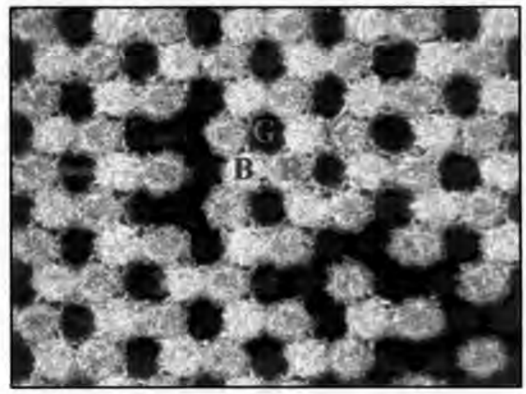
Upon an addition of the buffer (0.44 M) to the phosphor slurry, a formation of precipitate was observed. Furthermore, the specific gravity and viscosity were not in an adjustable range. Utilization of lower concentration buffer solution (0.067 M) resulted in a large increase of the slurry volume and again the specific gravity and viscosity of the slurry became uncontrollable. Thus, it is impossible to make screen coating from the phosphate buffered slurry. Only PVA formed precipitate, when the solutions of ADC, PVA and all surfactants were individually tested with the buffer solution. This may due to the high ionic strength of the buffer solution.

4.1.2 By disodium citrate and NaOH buffer solution pH 6.5

Although citrate buffer solution was compatible with the slurry, no precipitate formed, the coating results were disappointing. Green dots were not adhered or formed. Furthermore, blue and red dots were also detached from the panel. Figure 4.1 shows poor phosphor dots adherence pattern resulted from this buffered green slurry.



a



b

Figure 4.1 Poor phosphor dots adherence obtained from disodium citrate and NaOH buffered slurry after 100% exposure **a**) 7.5X magnification photo of some missing trios (group of blue, green and red dots) **b**) 50X magnification of **a**)

A major reason of poor green phosphor adherence is likely to be due to the additional carboxylate ions from disodium citrate buffer solution that caused a reduction of degree of crosslinking.

Other buffers might be considered for slurry in the future if they could be compatible to slurry and stabilize pH along the production. However the choices of good buffers are limited to the following requirements.

1) No halides

2) No heavy metal elements

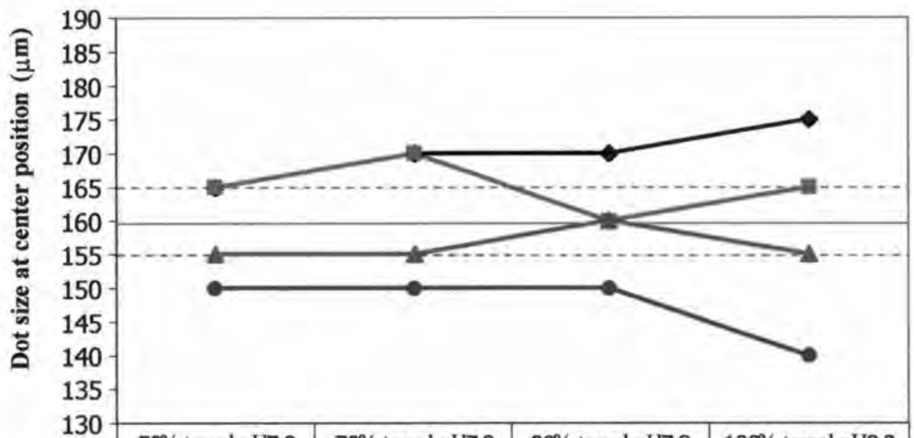
3) Not causing precipitation of phosphor slurry

4) Low volume required to stabilize pH of slurry

5) Polymeric carboxylate compounds might be able to use for new trail carboxylate buffer.

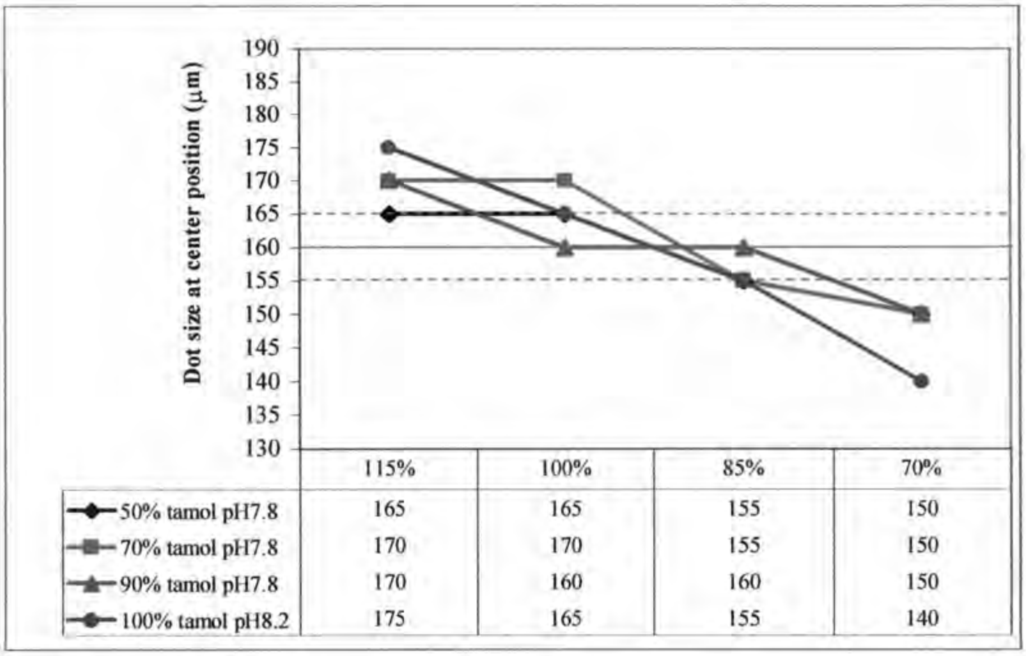
4.2 Screen qualities from reducing the amount of sodium polyacrylate (tamol) solution

It was noted from the above experiment that surfactants used in the phosphor slurry should already act like a buffer solution. The effect of the reduction of tamol to the slurry pH and the screen qualities was thus investigated.



	50% tamol pH7.8	70% tamol pH7.8	90% tamol pH7.8	100% tamol pH8.2
115%	165	170	170	175
100%	165	170	160	165
85%	155	155	160	155
70%	150	150	150	140

a



	115%	100%	85%	70%
50% tamol pH7.8	165	165	155	150
70% tamol pH7.8	170	170	155	150
90% tamol pH7.8	170	160	160	150
100% tamol pH8.2	175	165	155	140

b

Figure 4.2 a) Effect of the tamol amount to the dot sizes at center position

b) Photosensitivity lines from the effect of tamol amount (the grey dashed lines indicate the specification size (160 ± 5 μm))

From Figures 4.2a and 4.2b, the reduction of tamol from 100% to 50% could change pH of the slurry slightly, from 8.2 to 7.8. Dot sizes tended to be affected by the amount of exposure as the higher exposure the larger the dot sizes.

The interesting note is that dot size of 100% tamol serves as the maximum diameter size at 115% exposure and the minimum size at 70% exposure. At 50% tamol, the dot sizes became the least sensitive to the amount of exposure, however, many pin holes and poor sharpness were observed (Table A4.4). The best condition appeared to be at 90% tamol since the dot sizes met the specification even when the amount of exposure was reduced to 85%.

Poor phosphor film adherence was observed in all levels of tamol used at 85% and 70% exposure (Tables A4.1-A4.4). In color analysis, all colors of all screens are acceptable.

This experiment showed that tamol can be reduced by 10% to improve the photosensitivity. This should also lead to the cost saving from daily slurry preparation (about 15.2 KBht/year of saving).

4.3 Screen qualities from slurry pH adjusted by using sulfuric acid and ammonium hydroxide solution

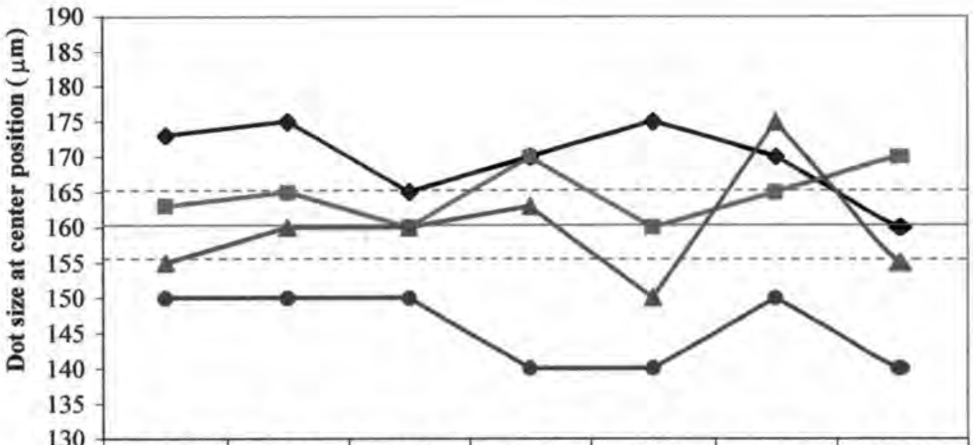
Sulfuric acid and ammonium hydroxide solution were compatible with the slurry, although, at some pH, high volume of sulfuric acid solution was needed (Table 3.11). Their specific gravity and viscosity were adjustable and coating results were acceptable. The experiments were done two times and the results from dot size measurement are shown in Table 4.1.

Table 4.1 Dot sizes at center/corner position resulted from slurry pH controlled at 6.0-9.0 by using 0.1 M sulfuric acid and 13.4 M ammonia solution

pH		% Exposure/ dot size (center/corner) (μm)			
		115%	**100%**	**85%**	**70%**
pH 6.0	**#1**	173/163	163/156	155/150	150/138
	#2	180/175	165/56	165/160	152/139
pH 6.5	**#1**	175/171	165/161	160/151	150/148
	#2	174/166	166/163	160/149	150/145
pH 7.0	**#1**	165/161	160/159	160/148	150/139
	#2	172/169	165/160	165/152	157/138
pH 7.5	**#1**	170/163	170/159	163/154	160/146
	#2	170/168	163/158	159/154	156/139
pH 8.0	**#1**	175/161	160/153	150/144	140/143
	#2	166/165	164/157	158/145	152/134
pH 8.5	**#1**	170/161	165/158	175/153	150/135
	#2	171/165	163/157	153/150	139/137
pH 9.0	**#1**	160/155	170/158	155/148	140/128
	#2	171/161	168/156	157/141	152/140

The measured dot sizes from both experiments were rather different. The major causes were discussed in result consideration below.

Dot sizes obtained from slurry pH 6.0-9.0 in the 1st experiment were plotted and found that the results were rather fluctuated and difficult to interpret.



	pH6.0	pH6.5	pH7.0	pH7.5	pH8.2	pH8.5	pH9.0
115%	173	175	165	170	175	170	160
100%	163	165	160	170	160	165	170
85%	155	160	160	163	150	175	155
70%	150	150	150	140	140	150	140

Figure 4.3 Effect of slurry pH to the dot sizes at center position at different amounts of exposure in the 1st experiment (the grey dashed lines indicate the specification size (160 ± 5 μm))

Figure 4.3 shows that the dot sizes tended to be depended on the amount of exposure as aforesaid in the results from the previous experiment, the reduction of tamol (Figure 4.2). Slurry pH 7.0 appeared to give the best results since good dot adherence was achieved and the dot sizes met the specification at the exposure levels of 85-115%. Other pH gave the poorer results especially for slurry pH 6.0

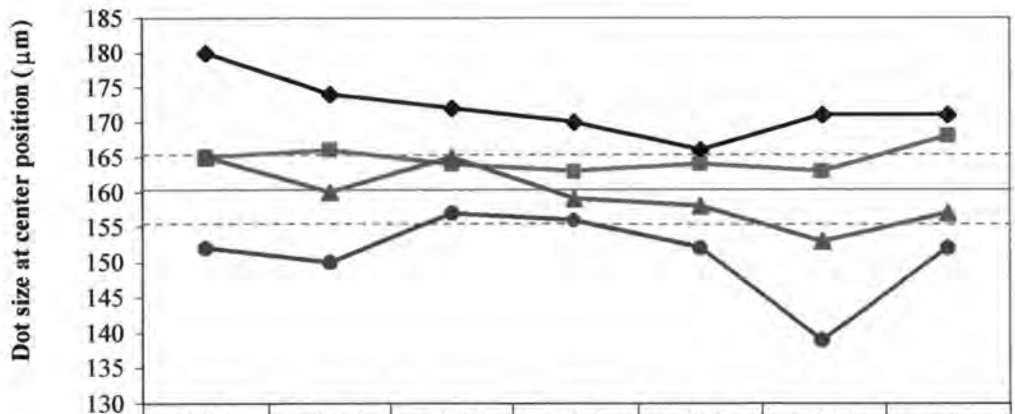
that some phosphor dots peeling off in all exposure amounts (Tables B4.1-B4.7). However, the following cautions needed to be addressed in applying these results.

1. The test at various pH were done on different days of production. The differences in inside temperature, water pressure of development after exposure, lamp capacity from exposure machine, and exposure's filter correction, were inevitable.

2. The tested screen were coated with all three colors (blue, tested green and red) that made it quite difficult in measuring the green dot sizes precisely due to the overlapping of the blue and red dots.

3. Other ambient parameters, for examples temperature, humidity, machine start/stop effect, were different.

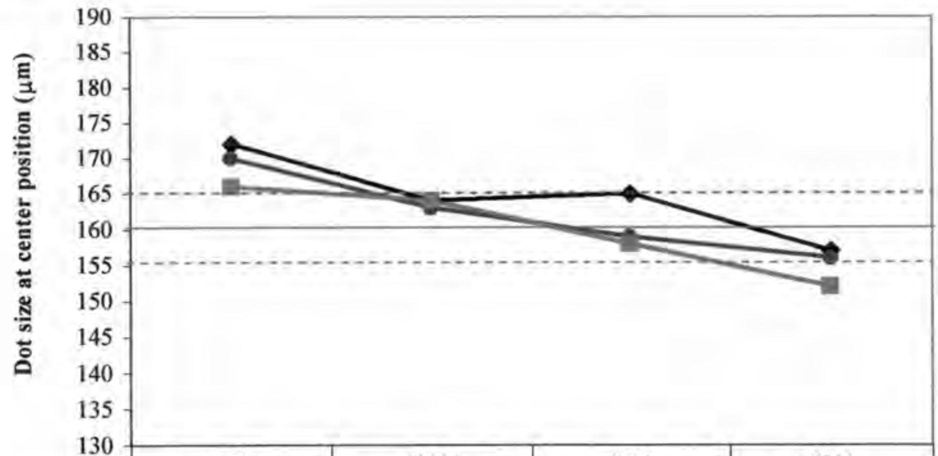
Thus the experiment was again confirmed to obtain more reliable results. The 2nd experiment was done in one day and only green color was coated. The results from this experiment seemed to be less fluctuated than those from the 1st experiment.



	pH6.0	pH6.5	pH7.0	pH7.5	pH8.2	pH8.5	pH9.0
115%	180	174	172	170	166	171	171
100%	165	166	164	163	164	163	168
85%	165	160	165	159	158	153	157
70%	152	150	157	156	152	139	152

Figure 4.4 Effect of slurry pH to the dot sizes at center position at different amounts of exposure in the 2nd experiment (the grey dashed lines indicate the specification size (160 ± 5 μm))

From Figure 4.4, the slurries with the pH between 7.0-8.2 gave the dot sizes within the specification even when the exposure amount was decreased, while at other pH range, some dot sizes were clearly out of the specification. Photosensitivity lines and the screen qualities obtained from slurry pH 7.0-8.2 were further compared closely (Figure 4.5, Tables C4.3 - C4.5).



	115%	100%	85%	70%
pH7.0	172	164	165	157
pH7.5	170	163	159	156
pH8.2	166	164	158	152

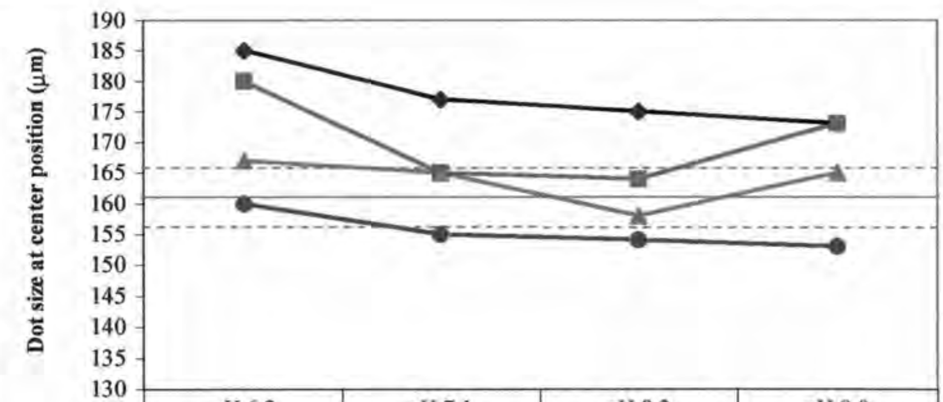
Figure 4.5 Photosensitivity lines at the optimum slurry pH 7.0-8.2 at center position in the 2nd experiment (the grey dashed lines indicate the specification size (160 ± 5 μm))

From Figure 4.5, slurry pH 7.0-8.2 displayed similar photosensitivity, however the slurry pH 7.0 seemed to be the best condition since 1) the dot sizes were not changed much especially when exposure amount was decreased from 100% to 70% 2) dot sizes met specification at the lower exposure (70%) 3) better sharpness was observed at 85% and 70% exposure and 4) less trouble area of poor film adherence was observed (Tables C4.3-C4.5). Photosensitivity of pH 7.5 was nearly same pH 8.2 but slightly better.

There were poor phosphor film adherence observed to all pH conditions at the exposure amounts of 85% and 70%. The poorest adherence was found from slurry pH 6.0, 8.5 and 9.0. (Tables C4.1-C4.7). The slurries with too low pH or high pH generated trouble in screening especially after development for the unexposed green dots. In the screening process, the slurries should thus be controlled at pH range of 7.0-8.2.

It was observed that, at 115% exposure, the dot sizes followed the Ozawa's theory for photocrosslinking process by ADC[2] (Figure 4.4). The higher concentration of $HCrO_4^-$ at lower pH could lead to faster and more extensive crosslinking resulting in larger dot sizes. At lower exposure, however, this trend seemed to be innoticable. Presumably, the lower exposure amount was not enough to deplete all the H_3O^+ ion from the reaction mixture. In summary of the 2nd experiment, slurry pH 7.0 gave better results than the routine slurry (pH 8.2) (Figure 4.5, Tables C4.3 and C4.5).

The results from the 2nd experiment were confirmed in the 3rd experiment by coating with the slurries composition as shown in Table 3.12. The total volumes of the slurry pH 6.2 – 9.0 were controlled to be the same by decreasing DI water in order to keep the concentration of all components to be constant. Therefore the effect on dot size and screen qualities would depend only on the pH. The volumes of acid and base used were calculated based on the results from the 2nd experiment to obtain the approximated pH of 6, 7, 8 and 9 (Table 3.12). The results were plotted and shown in Figure 4.6 and Tables D4.1 – D4.4.



	pH 6.2	pH 7.1	pH 8.2	pH 9.0
115%	185	177	175	173
100%	180	165	164	173
85%	167	165	158	165
70%	160	155	154	153

Figure 4.6 Effect of slurry pH to the dot sizes at center position at different amounts of exposure in the 3rd experiment (the grey dashed lines indicate the specification size (160 ± 5 μm))

The results agreed with the 2nd experiment in several aspects (Figure 4.4). Slurry pH 7.1 and 8.2 gave dot sizes within or close to the specification at the exposure level of 70-100%. Slurry pH 7.1 was slightly better than pH 8.2 (routine slurry) since it gave the constant dot size even when the exposure amount was decreased from 100% to 85%. At 85% exposure, pin hole and sharpness obtained from slurry pH 7.1 were also slightly better than those obtained from slurry pH 8.2 although they both gave poor phosphor film adhesion. At 115% exposure, the dot sizes tended to decrease with the increasing pH. For the alkaline slurry (pH 9.0), it produced poor dot sharpness and small dot sizes at the corner positions (see Table D4.4 and Tables D4.1-D4.3 for comparison) although acceptable film adherence was observed at 100% and 115% exposure (Table D4.4). This might be because some surfactants used in slurry composition worked better in alkaline than in the acid condition.

The screen qualities of finished tubes obtained from slurry pH 7.0 and 7.5 from the 2nd experiment were also tested to compare with the typical tubes. Results are shown in Table 4.2.

Table 4.2 Screen qualities obtained from slurry pH 7.0, 7.5 and typical tube

Items	Tube from slurry pH 7.0	Tube from slurry pH 7.5	Typical 14VCDT tube[a]
1. Green dot size (μm)	172/162	170/160	170/163
2. Screen color	Normal	Normal	Normal
3. Pin hole	Normal	Normal	Normal
4. Sharpness	Normal	Normal	Normal
6. CB (%)	94.9	93.9	91.9
7. FLO (R, G, B) (Cd/m^2)	30.5, 110.2, 14.6	30.7, 109.7, 14.3	29.9, 107.9, 13.8
8. WU level	5.0	4.5	4.5

From tube quality, it was found that screen quality from 3 conditions were not much different. However, good WU level and corner brightness were observed from slurry pH 7.0 tube.

Note : [a] Refer to TDDT-QAD monthly report during May 2000 (PH3).

From this experiment, we can improve the screen qualities obtained from the phosphor slurry by adjusting the pH to about 7.0. We can also increase the crosslinking reaction by lowering the slurry pH to supply H^+ for photoreaction of $HCrO_4^-$ as mentioned above at exposure amount 115% however the phosphor particles did not adhere well to the panel substrate at the lower exposure. The results clearly indicated that maximization of concentration of $HCrO_4^-$ in CDT phosphor slurry was not the only factor to be concerned in the screening process, even though the photoreaction of the PVA-ADC phosphor slurry in screen is essential for hardening of the phosphor film. Poor adhesion of phosphor particle in acid slurry (pH 6.0) could be due to 1) the faster hardening phosphor film preventing the UV light from reaching the bottom of PVA-phosphor screen on which the particles must adhere 2) acid might convert the carboxylate group of some surfactants to carboxylic group resulted in lower effectiveness of the surfactants in supporting the film adherence to the glass of screen.